Supporting Information

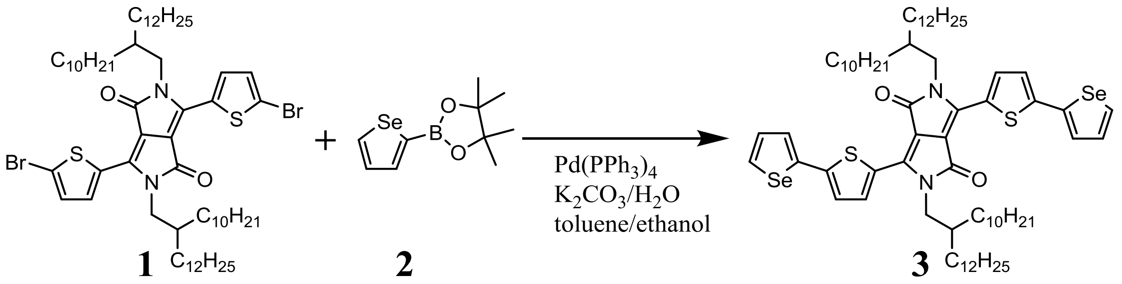
High-Mobility Terselenophene and Diketopyrrolopyrrole Containing Copolymer in Solution-Processed Thin Film Transistors

Min Ju Cho,*♦ Jicheol Shin,♦ Seung Hee Yoon, Tae Wan Lee, Matinder Kaur, Dong Hoon Choi*

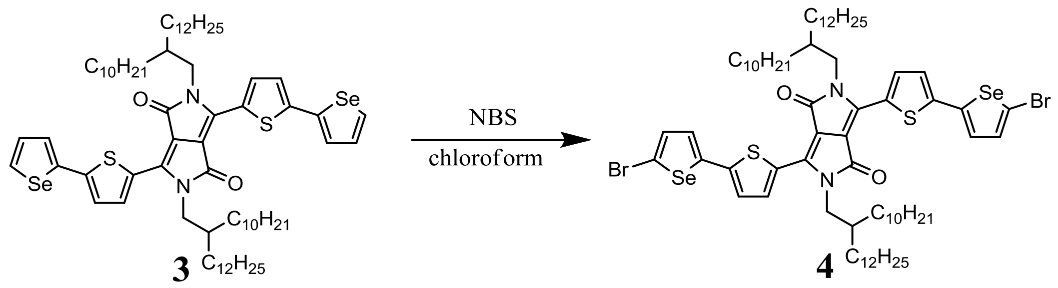
Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, 136-701 Seoul, Korea.
E-mail: dhchoi8803@korea.ac.kr;chominju@korea.ac.kr
♦*: equally contributed to this work*

Synthesis of Materials

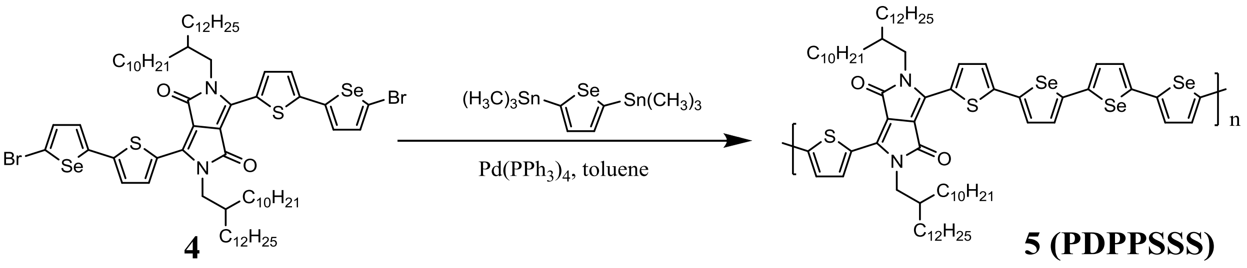
General: All reagents were purchased from Sigma-Aldrich Co. and used without further purification, unless stated otherwise. Reagent grade solvents used in this study were freshly dried under standard distillation methods. Compound **1**, **2**, and bis(trimethylstannyl)selenophene were synthesized according to literatures.[S1-S3]



***Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3)*:** To a solution of compound **1** (1.131 g, 1.00 mmol) and tetrakis(triphenylphosphine)palladium (0) (70 mg, 0.1mmol) in toluene (15 mL) were added ethanol (5 mL) solution of 4,4,5,5-tetramethyl-2-(selenophen-2-yl)-1,3,2-dioxaborolane (**2**) (0.65 g, 2.5 mmol) and aqueous 2M sodium carbonate (5 mL) at room temperature under argon atmosphere. The mixture was heated at 90 °C for 24 h and cooled to room temperature. The reaction mixture was poured into water and extracted with toluene. The organic phase was dried over $MgSO_4$. It was purified by silica-gel chromatography (eluent: dichloroethane: n-hexane, 1:3) to yield 1.04 g (84 %) of dark green powder. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.91 (d, J = 4.0 Hz, 2H), 8.01 (d, J = 4.0 Hz, 2H), 7.48 (d, J = 4.0 Hz, 2H), 7.30 (m, 2H) 7.25 (d, J = 4.0 Hz, 2H), 4.01 (d, 4H), 1.96 (m, 2H), 1.29–1.21 (m, 80H), 0.89–0.86 (m, 12H). MALDI-TOF MS exact mass calcd for $C_{70}H_{108}N_2O_2S_2Se_2$ [M^+] 1232.618, found 1232.042.



Synthesis of 3,6-bis(5-(5-bromoselenophen-2-yl)thiophen-2-yl)-2,5-bis(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4): To a solution of compound 3 (0.9 g, 0.73 mmol) in toluene (15 mL) was added *N*-bromosuccinimide (NBS) (0.26 g, 1.46 mmol) under argon atmosphere, and then the solution was protected from light and stirred at room temperature for 12 h. The mixture was poured into 200 mL of methanol and then filtered. The precipitate was purified by silica-gel chromatography (eluent: dichloroethane: n-hexane, 1:3) to yield 0.68 g (67 %) of dark green powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.86 (d, J = 4.0 Hz, 2H), 7.23 (d, J = 4.0 Hz, 2H), 7.16 (m, 4H), 4.01 (d, 4H), 1.92 (m, 2H), 1.29–1.21 (m, 80H), 0.89–0.86 (m, 12H). MALDI-TOF MS exact mass calcd for $C_{70}H_{106}Br_2N_2O_2S_2Se_2$ $[M+H]^+$ 1389.446, found 1389.501.



Synthesis of PDPPSSS (5): To a solution of compound **4** (0.278 g, 0.2 mmol) and 2,5-bis(trimethylstannyl)selenophene (0.091 g, 0.2 mmol) in toluene (15 mL) was added tetrakis(triphenylphosphine)palladium (0) (11.4 mg, 10.0 μmol) at room temperature under argon atmosphere. The mixture was heated at 100 °C and kept for 48 h. After cooling the mixture to room temperature, it was added to vigorously stirred methanol (300 mL), filtered and washed with methanol. The crude polymer was purified by Soxhlet extraction with acetone, hexane and chloroform. The chloroform was evaporated and then the polymer was precipitated in methanol, filtered and dried to give PDPPSSS polymer (0.21 g). (M_n = 47 kDa, M_w = 139 kDa, PDI = 2.96).

^{1}H NMR ($CDCl_3$, 300MHz), δ (ppm): δ 8.93 (br, 2 H), 6.75 (br, 6 H), 4.00 (br, 4 H), 1.21 (br, 82 H), 0.85 (br, 12H).

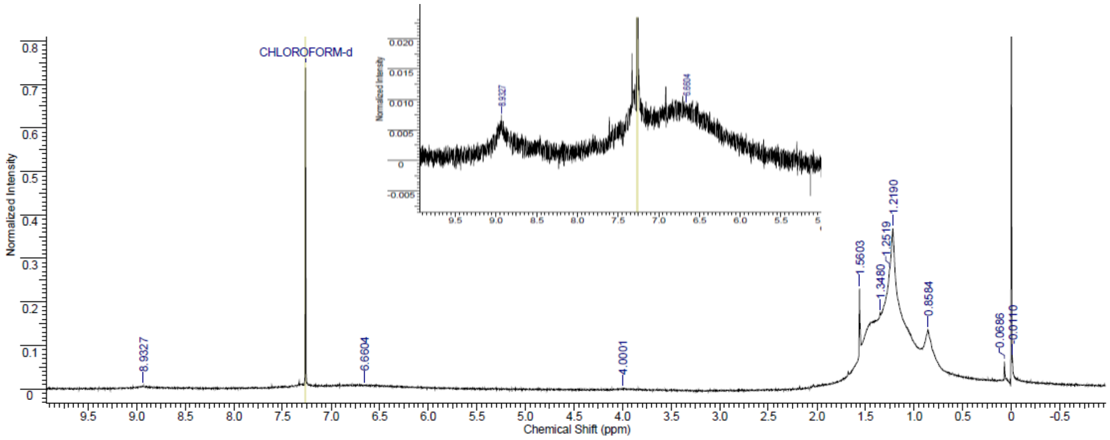
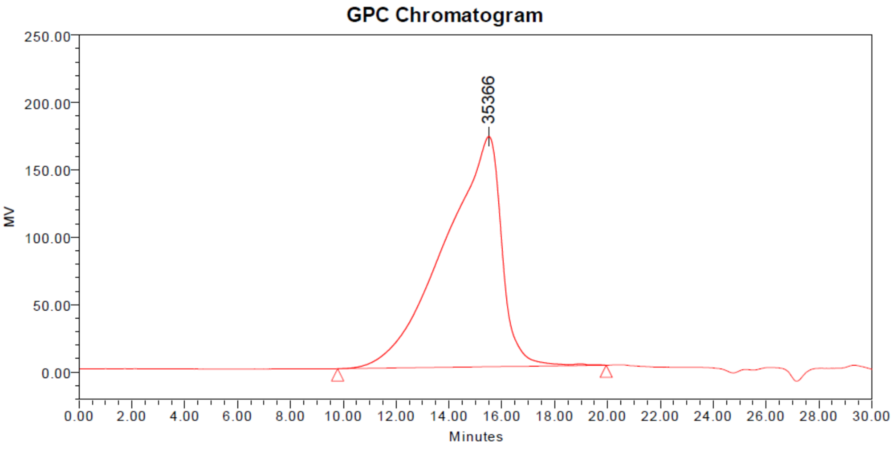


Figure S1. NMR spectrum of PDPPSSS in $CDCl_3$.



Peak Results

	Peak name	Mn	Mw	MP	Polydispersity	Mz	Mz/Mw	% Area	Retention Time
1	Peak1	47188	139808	35366	2.962799	477574	3.415920	100.00	15.511

Figure. S2. GPC chromatogram of PDPPSSS. *Chloroform as an eluent at a column temperature of 35 °C.

Instrumentation

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300MHz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. The molecular weight of the polymer was determined by gel permeation chromatography (Waters GPC, Waters 515 pump, Waters 410 RI, 2x PLgel Mixed-B) using polystyrene as the standard and chloroform as an eluent (T=35 ^{o}C). Atomic force microscopy (AFM, Advanced Scanning Probe Microscope, XE-100, PSIA) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the polymer films. The film sample was fabricated by spin-coating (2000 rpm, 30 sec) on *n*-octyltrichlorosilane (OTS)-treated silicon wafer followed by drying at 50 ^{o}C under vacuum (solvent: chloroform, conc. of the solution: 3 mg/mL).

Absorption spectra of samples in film and solution states were obtained using a UV-vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1100 nm.

OTFT Device Fabrication

For the characterization of TFT performance, top-contact/bottom-gate (TCBG) and bottom-contact/bottom-gate (BCBG) device geometries were employed. Surface modification was carried out with OTS to make hydrophobic dielectric surface. In the case of TCBG device, on OTS-treated heavily n-doped Si/SiO_2 substrate, thin films were spin-coated using chloroform solution (0.3 wt %) stirred for three days in room temperature (i.e. OTS-treated Si/SiO_2 substrate / PDPP-SSS)/Au). Source and drain gold electrodes were then thermally evaporated (100 nm) through shadow mask with channel width and length of 1500 μm and 100 μm, respectively. BCBG devices were also fabricated, having the configuration of OTS-treated Si/SiO_2 substrate /Au/ PDPPSSS. All the field effect mobilities were extracted in the saturation regime using the relationship $\mu_{sat}=(2I_{DS}L)/(WC(V_G-V_T)^2)$, where I_{DS} means saturation drain current, C is capacitance (~11.5nF cm^{-2}) of SiO_2 dielectric, V_G is gate bias, and V_T is threshold voltage. The device performance was evaluated in air using 4200-SCS semiconductor characterization system.

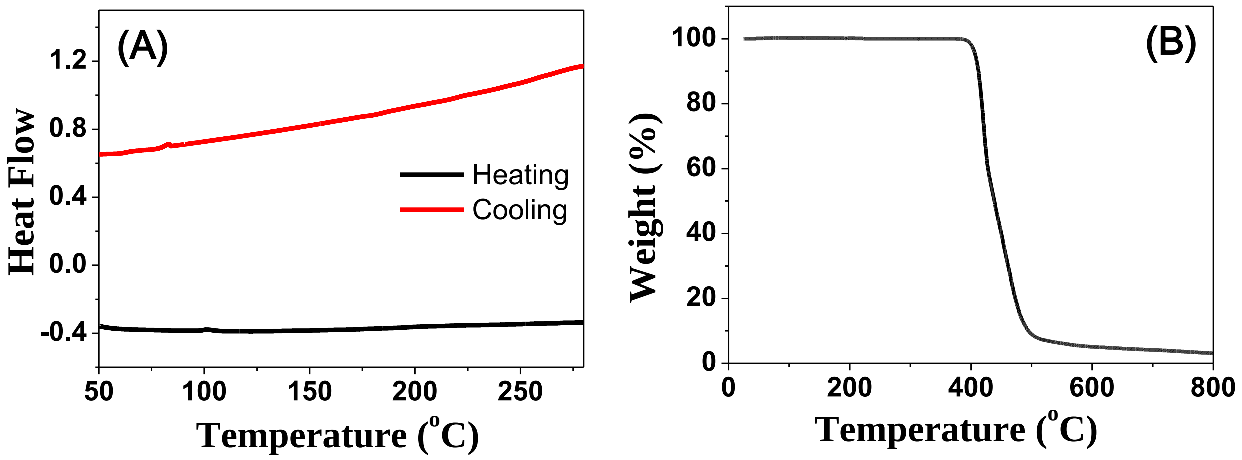


Figure S3. (A) Differential scanning calorimetry (DSC) and (B) thermogravimetric analysis (TGA) curve for PDPPSSS.

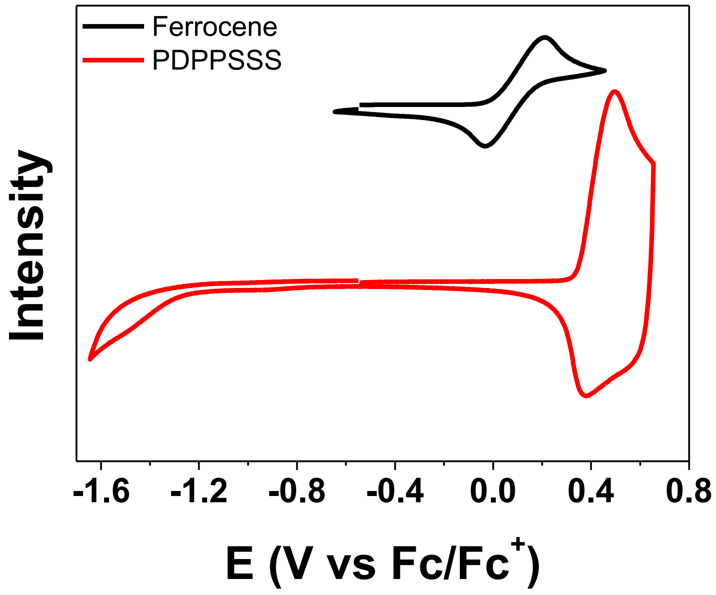


Figure S4. Cyclic Voltammogram (CV) of PDPPSSS. *film on Pt plate electrode.

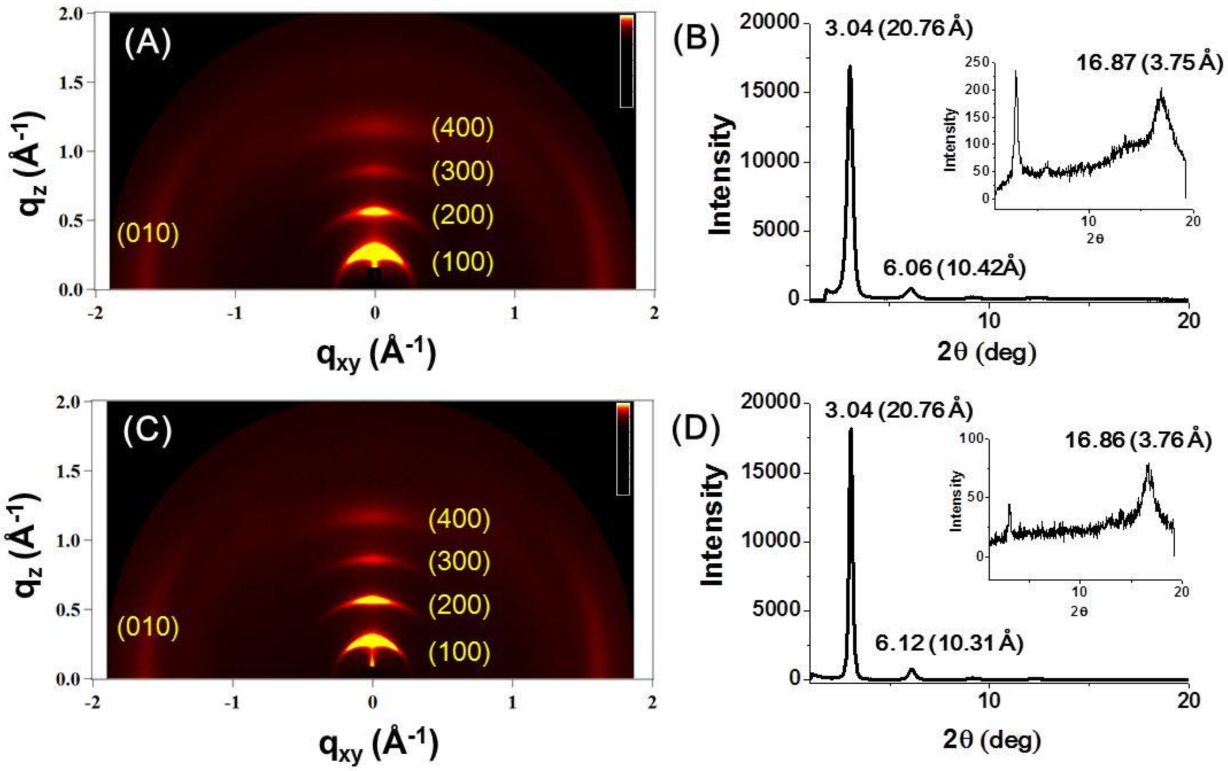


Figure S5. (A), (C)**:** 2-D GI-XRD patterns for PDPPSSS thin films on OTS-treated SiO_2/Si substrate. (B), (D): 1-D out-of-plane and in-plane (inset) profiles. (A) and (B) pristine film. (C) and (D) thermally annealed film ($T_{\text{annealing}}$ = 200 ^{o}C).

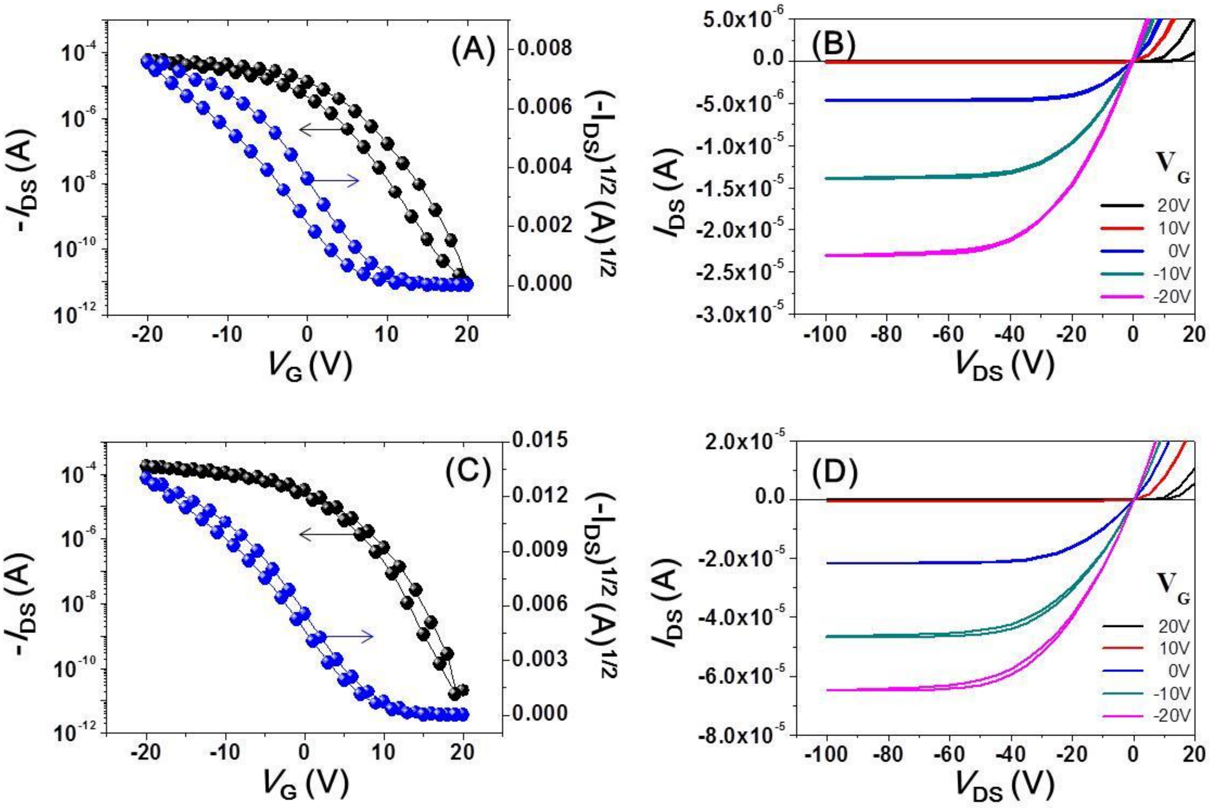


Figure S6. Device performances of BCBG-TFT made of PDPPSSS. (A) transfer and (B) output curves of the TFT device fabricated with pristine film; (C) transfer and (D) output curves of the TFT device fabricated with thermally annealed (200 °C for 10 min) film. *OTS-SiO_2/Si gate insulator; the device performances were measured in air. V_{DS} = -100 V.

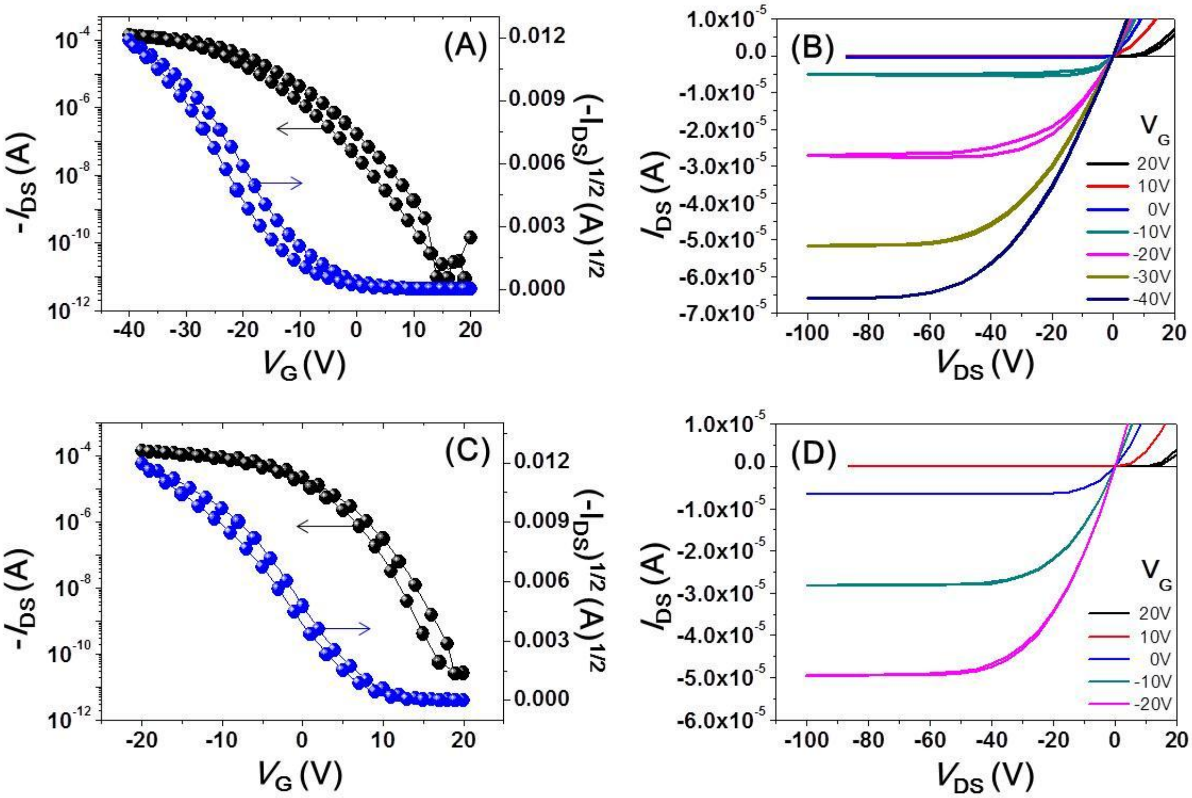


Figure S7. Device performances of TCBG-TFT made of PDPPSSS. (A) transfer and (B) output curves of the TFT device fabricated with pristine film; (C) transfer and (D) output curves of the TFT device fabricated with thermally annealed (200 °C for 10 min) film. *OTS-SiO_2/Si gate insulator; the device performances were measured in air. V_{DS} = -100 V.

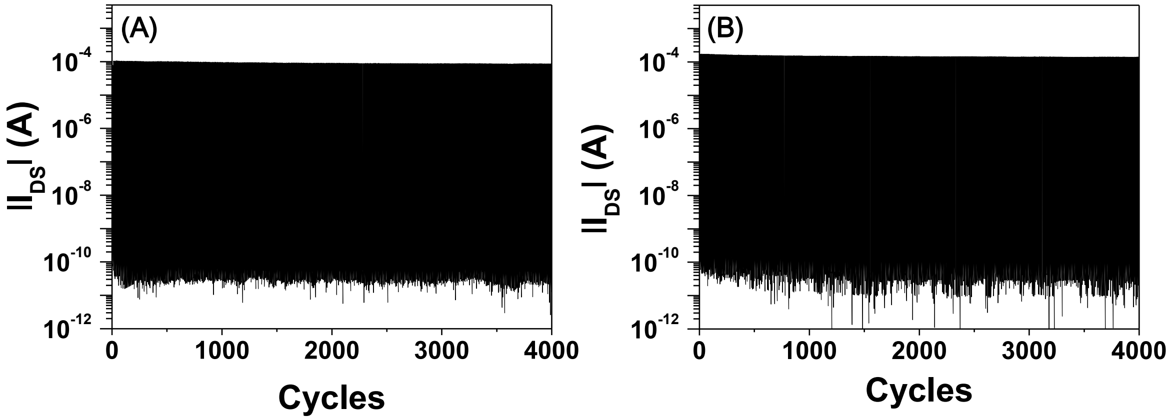


Figure S8. Operational stability of the PDPPSSS-based BCBG (A) and TCBG-TFT (B) device during current on/off cycle test in air (4000 cycles, at V_{DS} = -100 V, V_G = 20 V (off) and V_G = -20 V (on)). *TFT made from thermally annealed film. ($T_{annealing}$ = 200 °C for 10 min).

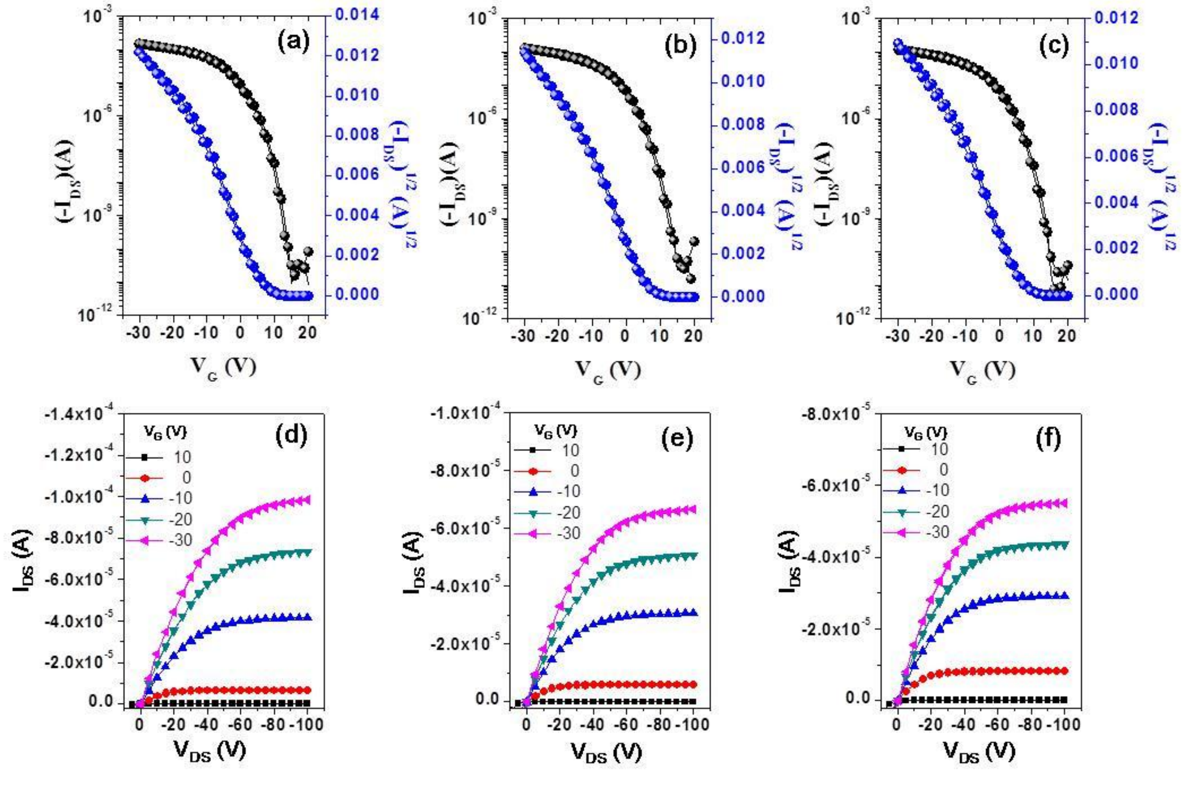


Figure S9. Transfer (a, b, and c) and output (d, e, and f) curves of BCBG-TFTs made of PDPPSSS film with the polymer layer. *Active channel layer, (a), (d): PMMA/ PDPPSSS/OTS-SiO_2; (b), (e): P(α-MS) /PDPPSSS/OTS-SiO_2; (c), (f): PTAA/PDPPSSS/OTS-SiO_2.

References

S1. S. Cho, J. Lee, M. G. Tong, J. H. Seo, and C. Yang, *Adv. Funct. Mater*., 2011, **21**, 1910.

S2. S. Haid, A. Mishra, C. Uhrich, M. Pfeiffer, and P Bäuerle, *Chem. Mater*., 2011, **23**, 4435.

S3. S. Haid, A. Mishra, M. Weil, C. Uhrich, M. Pfeiffer, and P. Bäuerle, *Adv. Funct. Mater*., 2012, **22**, 4322.